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SUPPLY OF REACTANTS FOR REDOX BULK ENERGY STORAGE SYSTEMS

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SUMMARY

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A review was made of the present world resources, reserves, production and costs of reactant materials iron, chromium, titanium and bromine for proposed Redox Flow Cell Bulk Energy Storage Systems. Supplying required materials for multimegawatt hour systems appears to be feasible even at current production levels. Iron and chromium ores are the most abundant and lowest cost of the four reactants. Chromium is not a domestic reserve, but Redox system installations would represent a small fraction of U.S. imports. Vast quantities of bromine are available, but present production is low and therefore cost is high. Titanium is currently available at reasonable cost, with ample reserves available for the next fifty years.

INTRODUCTION

The emphasis upon energy conservation has stimulated the search for cost effective electrical energy storage schemes to improve the operating efficiency of electric utilities. Many types of electrochemical energy storage systems have been proposed for this purpose with serious development being initiated on several of them (ref. 1). The primary need for bulk energy storage is to enable electric utility companies to meet the peak energy demands of large metropolitan areas. Energy storage also allows for more efficient utilization of the base load generating equipment. Also, the success of solar photovoltaic and wind turbine generators as alternate energy sources is very dependent upon suitable energy storage.

One electrochemical system for bulk energy storage, the Redox Flow Cell, has been under development during the last four years at the Lewis Research Center (ref. 2). A schematic diagram of the system is shown in figure 1. Energy is stored in two soluble reactant fluids. The two separated fluids flow through an electrochemical conversion section where oxidation of one fluid occurs on one side of an ion selective membrane and reduction of the other fluid occurs on the other side to produce electricity. To charge the system, current is supplied by the power source, for example, electric utility company, solar or wind generator. Initial work has

shown that the Redox system could meet the criteria established for a bulk energy storage system (refs. 3 and 4). The Redox system has been evaluated experimentally as a storage system for a solar photovoltaic energy system (ref. 5). Although limited in nature, this work indicated good compatibility and interfacing characteristics of the two systems.

Bulk energy storage systems based on electrochemical concepts require large facilities as well as large quantities of reactive materials. The Redox system uses acid soluble reactants which include iron, chromium, titanium and bromine. Two promising systems are the iron-chromium and bromine-titanium combinations in acidic chloride solution. Storage capacities of Redox systems could range from multi-kilowatt-hour sizes for solar applications to multi-megawatt-hour sizes for electric utility energy storage systems.

The purpose of this study is to assess the availability and cost of the raw materials for use in large redox plants. The impact of supplying redox reactants on current production is also estimated. Cost is based on raw materials only and does not include processing steps to prepare the desired chemical form. Known deposits of material in the Earth's crust which could be mined if production were economically feasible are called resources. Material which can be produced economically with current technology is referred to as reserves. World production was used as the basis for the impact on production. An important consideration is the principle location of the raw material. Political situation with the countries involved and balance of payments must be considered, but the impact assessment of these factors in detail is beyond the scope of this report.

Redox system costs, sizing and modeling studies have determined the quantity of material required for a particular system (refs. 3 and 4). In this study, the effect on production was based on a 20 MW, 100 MWH, 60 percent utilization system. This size of system is typical of as a storage facility for a utility company with daily cycle storage requirements.

RESULTS

Statistical information was obtained from references 6 and 7. Results of the study are tabulated in table I. The supply and cost of the three metal

reactants, iron, chromium and titanium were based on their ores. Iron ore contains about 30 to 70 percent iron. Chromite ore, the source of chromium, contains between 22 to 38 percent chromium. Ilmenite and rutile ores are the sources of titanium. Ilmenite ore concentrates contain about 32 percent titanium. Rutile ore concentrates contain about 60 percent titanium. Bromine is produced in the elemental state, Br_2 , or as salts such as NaBr , KBr and CaBr_2 .

Iron ore resources are the most abundant of the four reactants with 896×10^9 tons of minable ore. World reserves are estimated at 32 percent of the resources. The U.S.A. has ~14 percent of the world's iron ore resources. Domestic resources could meet forecast demand through the year 2000. However, due to advantages in price, quality, transportation costs of some foreign ores and investments by U.S. steel producers in foreign mining projects, imports of ore are expected to continue.

World chromium resources are considered to be abundant with an estimated 18×10^9 tons of chromite ore available. However, domestic resources of chromium are small and low grade. Domestic production of chromium was curtailed in 1961. Most of the chromite ore is located in the Republic of South Africa and Southern Rhodesia. World reserves of chromium are about 15 percent of the resources and are predicted adequate to meet the demand for the foreseeable future.

Ilmenite ore supplies 85 percent of the world's demand for titanium. The remainder comes from rutile. World resources of ilmenite total 3.7×10^9 tons of concentrate. The U.S.A. has major ilmenite resources or about 16 percent of the world resources. In 1976 the U.S.A. imported 44 percent of its ilmenite. World ilmenite reserves are 21 percent of the resources. Other major locations of ilmenite are in Canada, Norway and South Africa. Ninety-nine percent of the domestic ilmenite production is used for titania pigment production.

Rutile ore is much less abundant than ilmenite. World rutile resources are estimated at 220×10^6 tons of concentrate with about 3 percent located in the U.S.A. Australia is the source for about 90 percent of the world's supply. The U.S.A. has one rutile producing mine located in Florida. The U.S.A. is 90 percent dependent on foreign markets for rutile. Rutile is preferred to ilmenite because of its higher titanium content and less

processing waste. Eighty percent of the known world rutile resources can be classed as reserves.

Virtually unlimited amounts of bromine are available from sea water and brine wells. There are no estimates for bromine resources or reserves. The Dead Sea in Israel is estimated to contain one billion tons of bromine. Major U.S.A. sources are from brine wells in Arkansas and Michigan.

1976 World and U.S.A. Production and the price per ton of the Fe, Cr, and Ti ores and bromine are shown in table I. World iron ore production is the largest of the four reactant materials at 987×10^6 tons. The U.S.A. produced 90×10^6 tons or 9 percent of the world production. 1976 price was \$18/ton. Chromite ore world mine production was 9.49×10^6 tons. Production of chromite ore was resumed in the U.S. in 1976, but tonnage figures were withheld and are likely insignificant. Imports supplied 90 percent of U.S. chromium demand with the balance coming from reclamation of scrap. South African ore price was \$35/ton for 1976 but is estimated at \$54/ton for 1977. World production of the titanium ores ilmenite and rutile as concentrates, were 4.28×10^6 and 0.44×10^6 tons. U.S. ilmenite production was 0.65×10^6 tons or about 15 percent of the total. Figures of the U.S. production of rutile were withheld but can be estimated at about 10 percent. Price of ilmenite and rutile ore concentrates were \$49 and \$510/ton, respectively. Rutile price for 1977 is estimated to decrease to about \$366/ton. World bromine production was 0.327×10^6 tons with 0.22×10^6 tons (67 percent) produced by the U.S.A. Bromine price was \$600/ton.

The last two columns of table I show the impact on world production if one hundred, 100 MWH redox energy storage plants were brought into operation and the ore cost per 1000 amp-hr (AH) of energy storage. (One hundred plants is an estimate of the number of battery systems which could be produced cost effectively per year by four battery companies dedicated to electrochemical storage system fabrication (ref. 8).) The quantity of reactant material required was based on a system operating on a daily cycle under discharge conditions of 20 MW for 5 hours with a 60 percent utilization of reactants. Using these criteria, 7.77×10^6 moles (equivalent to 445 tons chromium metal, 479 tons iron metal, 410 tons titanium metal

and 1030 tons bromine) of each reactant is required for these single electrode transfer reactions. Calculations for ore requirements were based on iron ore containing 51.5 percent iron, chromite ore containing 30 percent chromium, ilmenite ore concentrate containing 32 percent titanium and rutile ore concentrate containing 60 percent titanium. Bromine calculations were based on a 50 percent excess required due to the formation of the tribromide ion, Br_3^- ($\text{Br}_2 + \text{Br}^- = \text{Br}_3^-$) in the charged state. Bromine raw material was assumed pure.

Using these basic assumptions the percent of the World 1976 Production was calculated for each reactant.

Iron ore required for 100 plants would be 0.0094 percent of the 1976 World Production. Iron ore cost is \$0.08/1000 AH. Chromite ore required is 1.6 percent of 1976 World Production with an ore cost of \$0.25/1000 AH. Using ilmenite ore as the source of titanium supply would require 3.0 percent of the one year production. With rutile as the titanium source, 15.5 percent of the 1976 World Production would be required to supply 100 plants. Ore costs for ilmenite and rutile would be \$0.30 and \$1.67/1000 AH capacity, respectively. Bromine needed for 100 plants would be 31.4 percent of the world production and cost estimate is \$2.97/1000 AH.

DISCUSSION

The current availability of the four reactant materials can be determined from the world reserves. The world reserves for iron ore, chromite ore and ilmenite ore are 32, 15, and 21 percent, respectively, of the world resources. For rutile ore, 80 percent of the resources are considered reserves. Comparison of the reserves for iron ore, chromite ore, ilmenite ore concentrate and rutile ore concentrate are given by the following ratios: 1619:15:4:1. Bromine could not be ranked since quantitative figures were not available. Either recovery technology must be advanced or prices increased to make mining of the resources economically feasible.

The rate at which reserves are being consumed can be estimated from the 1976 world ore production (see table I). In 1976, iron ore, chromite, ilmenite and rutile ore production was 0.35, 0.35, 0.56, and 0.25 percent, respectively, of the reserves. At this rate of consumption, iron and chromium reserves would last for about 300 years, ilmenite about 200 years and rutile ore for about 400 years. However, even if the production increases at the rate of 2 percent/year (a reasonable rate of increase) after fifty years about 70 percent of the world reserves of iron ore and chromite, 52 percent of ilmenite, 78 percent of rutile and large amounts of bromine would still remain untouched. (Calculations made using standard compound interest formula.) There appears to be no significant depletion of any of the four reactant materials in the next fifty years. Anticipating that mining technology will improve in the next fifty years more of the resources will become reserves thereby increasing these percentages.

The quantity of reactant material required for one hundred, 100 MWH plants was compared to the 1976 World Production. The effect on iron, chromium and titanium from ilmenite production is small, at 0.0094, 1.6, 3.0 percent, respectively. The impact on the one year titanium from rutile and bromine production is more significant at 15.5 and 31.4 percent, respectively. However, if these 100 plants would be built over a ten year period, the demand would be within the scope of the 1976 production rate.

Ore prices have increased considerably during the past several years and are expected to continue increasing. Chromite ore prices have shown the largest increase in recent years. At the present time, chromium supply and price outlook is not favorable since the major producing countries are Southern Rhodesia and South Africa. Other chromite sources are the U.S.S.R., Phillipines and Turkey. Since the U.S.A. has an insignificant chromium production, it is more than 90 percent dependent on imports. Although the chromium price may increase more rapidly than the other reactants, it could still remain less expensive than titanium or bromine.

Considering the current status for supply and cost of the four redox reactants, iron and chromium are ranked most favorable. Iron supply and cost poses no foreseeable problems. At the present time chromium

import supply is ample and although there have been recent price increases, it is still an economical reactant material. The supply of bromine and titanium is also adequate. The supply of each could probably be readily increased if the market existed. The titanium industry has suffered due to cutbacks in aerospace activity and could use an additional market. The cost of both titanium and bromine are higher than iron and chromium, but would probably be reduced as production is increased.

CONCLUDING REMARKS

Iron ore is the most abundant and lowest cost of the four raw materials investigated. Supply and cost poses no problems since large ore deposits exist in the U.S.A. Chromite ore is considered abundant but the U.S.A. supply is 90 percent dependent on imports. Chromium resources are located primarily in South Africa and Southern Rhodesia. Chromium ore costs have increased rapidly in recent years, but still remains lower than titanium or bromine. The titanium ore, ilmenite, is available domestically although about one-half of the U.S.A. demand is imported. Rutile, a secondary titanium ore, supplies about 15 percent of the world's titanium ore demand. Ilmenite ore price is only slightly higher than chromite ore, but rutile is about seven times more than chromite. Although no quantitative estimates of bromine reserves are available, the recoverable amount is known to be large. Bromine price is highest of all reactants.

At the 1976 ore production level, raw materials required for one hundred, 100 MWH Redox plants would have a significant impact on only the rutile and bromine production. Iron, chromite, and ilmenite ore production would be relatively unaffected by the requirements of the one hundred Redox plants.

In summary, the raw materials necessary to supply reactants for Redox energy storage plants are available and reserves are adequate for at least the next fifty years. Iron and chromium are the most abundant, have the largest production and presently are lowest cost. Titanium and bromine are also relatively abundant, but lower production reflects higher materials costs.

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TABLE I. - SUPPLY AND COST OF RAW MATERIALS FOR POSSIBLE REDOX REACTANTS

[Data in million short tons.]

Reac-	Raw material	Principle raw material location	Resources		World reserves	1976 Production		1976 Raw material price \$/short ton	Percent ^a of 1976 world production	Ore cost \$/1000 AH
			World	U. S. A.		World	U. S. A.			
Fe	Iron ore	Worldwide	896×10^3	121×10^3	285×10^3	987	90	18	0.0094	0.08
Cr	Chromite ore	So. Rhodesia So. Africa	18×10^3	8	2.7×10^3	9.49	W ^b	^d 35	1.6	.25
Ti	Ilmenite ore ^c	So. Africa Canada U. S. A.	3.70×10^3	574	771	4.28	0.652	49	3.0	.30
	Rutile ore ^c	Australia	220	6	176	0.440	W ^b	510	15.5	1.67
Br	Sea water Brine wells	Worldwide	Virtually Unlimited		Unknown but large	0.327	0.220	600	31.4	2.97

^aBased on one hundred, 100 MWH plants/year.^bInformation withheld.^cAs concentrate. Ilmenite: 54 percent TiO_2 ; Rutile: 100 percent TiO_2 .^dSouth African ore.

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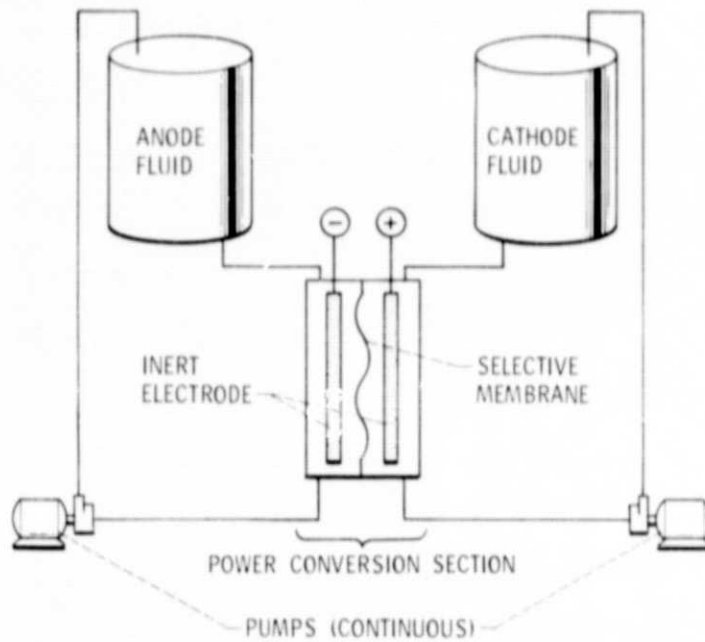


Figure 1. - Two tank electrically rechargeable redox flow cell.